

VOLUMETRIC POLYMERIZATION SHRINKAGE OF CONTEMPORARY COMPOSITE RESINS

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ABSTRACT

The polymerization shrinkage of composite resins may affect negatively the clinical outcome of the restoration. Extensive research has been carried out to develop new formulations of composite resins in order to provide good handling characteristics and some dimensional stability during polymerization. The purpose of this study was to analyze, *in vitro*, the magnitude of the volumetric polymerization shrinkage of 7 contemporary composite resins (Definite, Suprafill, SureFil, Filtek Z250, Fill Magic, Alert, and Solitaire) to determine whether there are differences among these materials. The tests were conducted with precision of 0.1 mg. The volumetric shrinkage was measured by hydrostatic weighing before and after polymerization and calculated by known mathematical equations. One-way ANOVA ($\alpha=0.05$) was used to determine statistically significant differences in volumetric shrinkage among the tested composite resins. Suprafill (1.87 ± 0.01) and Definite (1.89 ± 0.01) shrank significantly less than the other composite resins. SureFil (2.01 ± 0.06), Filtek Z250 (1.99 ± 0.03), and Fill Magic (2.02 ± 0.02) presented intermediate levels of polymerization shrinkage. Alert and Solitaire presented the highest degree of polymerization shrinkage. Knowing the polymerization shrinkage rates of the commercially available composite resins, the dentist would be able to choose between using composite resins with lower polymerization shrinkage rates or adopting technical or operational procedures to minimize the adverse effects deriving from resin contraction during light-activation.

Uniterms: Composite resins; Polymerization shrinkage.

INTRODUCTION

The formulation of composite resins has been modified during the past years with the purpose of improving their physical, mechanical and handling characteristics. Among the main factors related to the clinical outcome of composite resin restorations, the quality of the restorative material-tooth interfacial seal and absence of microleakage are definitely considered^{1,16}. This is largely determined by the degree of polymerization shrinkage of the composite resin and the quality of bonding to tooth structures²⁰. However, other critical factors are well known to contribute to the quality of marginal sealing, such as configuration factor, filling technique, bonding system and modulation of light-curing⁶.

Shrinkage is associated with the polymerization reaction in a complex way. The decrease in shrinkage strain can

sometimes be attributed to reduced binding in the polymer network caused by less conversion or to an increased flexibility of the materials. However, research in resin formulation has led to structural modification by the development of new acrylic molecules. The changes in the organic matrix of the composite resins, therefore, may contribute to the magnitude of polymerization shrinkage. The main component of most composite resins used in dentistry is BISGMA in its linear form¹⁸. The synthesis of BISGMA, by the addition of two molecules of glycidylmethacrylate to one bisphenol-A, results in a molecule with two free hydroxyl-groups, which are slightly hydrophilic. In order to make BISGMA hydrophobic, its structure has been modified by ethoxylation of bisphenol-A at various ethoxylation degrees and final methacrylation, which leads to a more hydrophobic molecule. Thus, less hydroxyl groups were present in the composite resin and

consequently the material became less susceptible to the absorption of liquids¹². Among other modifications, it can be mentioned the replacement of BISGMA and TEGMA of the organic matrix by an organic silicium compound known as Ormocers⁷, which is the acronym of ORganically MODified CERamic.

Several publications have determined the influence of polymerization shrinkage on composite resin restorations^{8,9,17}. Therefore, the purpose of this study was to analyze the magnitude of the volumetric polymerization shrinkage of 7 contemporary composite resins to determine whether there are differences among them. The null hypothesis is that no significant differences will be detected among the tested materials.

MATERIAL AND METHODS

Seven medium- and high-density hybrid composite resins were selected for this experiment: Two with organic silicium matrix, two with ethoxylated BISGMA and three with BISGMA (as declared by the manufacturers). The individual characteristics of the resins are described in Table 1.

The tests were carried out in a standard laboratory under controlled room temperature (23±3°C) and relative humidity (50±5%). A scale (mark AND A & D Weighing, series HR-200, the USA) accurate to 0.0001g and 0.05% was used. The weighing scale had two receptacles connected by a metallic brace. One receptacle was empty and the other was immersed in a beaker containing distilled water. The water level was kept 1 cm above the specimen⁵.

To perform the test, 1 g of composite resin, as recommended by ASTM: D792 specification², was placed in a Teflon split mould between two strips of siliconated polyethylene and pressed manually with two flat glass plates resulting in a thin disc (±1.0 mm thick). The plastic strips and the split mould were carefully removed and the resin was weighed in order to determine the mass of the resin in air (M1). The disc was carefully removed from the scale receptacle in air and was transferred to the receptacle immersed in water and weighed (M2). According to Puckett; Smith¹⁴, no alteration in the weight of resins occurs when they are submerged in water for up to 2 minutes before polymerization.

Five specimens of non-polymerized resins were separately weighed in air and water and the values were used to calculate the specific gravity (sp gr) of composite resins before polymerization. At the moment of each weighing, the water temperature was measured with a precision thermometer with accuracy of ± 0.1°C. For this water temperature the water density was used to calculate the specific gravity. The following equation was used: $sp\ gr = M1 / (M1 - M2 \times \text{water density})$, where: M1 = mass of resin in air and M2 = mass of resin in water

The specimen was removed from water, dried with absorbent paper and then polymerized with a light-curing unit (LED "Blue Star 1", Microdont, São Paulo, SP, Brazil) for 20 seconds with light intensity of 1250 mW/cm². After

polymerization, the same weighing procedure was repeated. The densities of the specimens were used to calculate the corresponding volumes as follows: $V1 = M1/D1$ and $V2 = M2/D2$, where: V1= volume of unpolymerized resin; V2= volume of polymerized resin; M1= mass of unpolymerized resin in air; M2= mass of polymerized resin in air; D1= density of unpolymerized resin; D2= density of polymerized resin

After obtaining the pre- and post-polymerization volumes of the specimens, the percentage of volumetric contraction was calculated as follows: $\%shrinkage = (V1 - V2 / V2) \times 100$.

One-way ANOVA ($\alpha=0.05$) was used to determine statistically significant difference in volumetric shrinkage among the tested composite resins.

RESULTS

Table 2 displays the means and standard deviation of percent volumetric shrinkage for each material. Suprafill and Definite presented the least volumetric polymerization shrinkage, both significantly different ($p>0.05$) when compared to the other composites. SureFil, Filtek Z250 and Fill Magic were not significantly different ($p<0.05$) from each other and presented intermediate volumetric shrinkage. Solitaire and Alert presented higher polymerization shrinkage and both were significantly different ($p>0.05$) from the other resins.

DISCUSSION

Studies on the matrix formation of the resin complex have shown that BISGMA is the main monomer and that the degree of conversion decreases with the increase of its proportion in the composition. The authors concluded that the decrease in the conversion rate due to the increase in BISGMA content does not decrease the magnitude of strength or hardness of the resin. Following the calculation according to the rules for mixtures to keep proportion in these co-monomers, the results can be relevant to clinical use.

BISGMA is present in most of formulations as the main part of the organic matrix of composite resins due to its low contraction rate when compared to other similar monomers. The high viscosity (628 Pa*s 25°C) of BISGMA indicates that there are less degrees of freedom in the BISGMA molecule than in the least viscous monomers. This leads kinetically to a low degree of conversion, thus resulting in a lower shrinkage. Due to its high viscosity, it requires dilution with other low-viscosity dimethacrylates such as the oligomers TEGMA (triethyleneglycoldimethacrylate) and EDGMA (ethyleneglycoldimethacrylate) or functional monomers, like HPMA (hydroxypropylmethacrylate) or aromatics, such as BISEMA (Bisphenol-A ethoxylated dimethacrylate) or BISMA (bisphenol-A dimethacrylate). As a consequence of polymerization, the resin system shrinks mainly because the intermolecular distance of the monomer molecules in the network shortens from 0.3-0.4nm to 0.15nm, when the double-bonds are polymerized to covalent main-

chain bonds^{11,13}.

Solitaire, a silicon-organic resin (ORMOCER), showed the highest shrinkage in the present study. In this case, the silicon-backbone is intrinsically connected to four acrylate monomer-groups. It is a tetrafunctional matrix with many crosslinking groups. This material has BISGMA (bifunctional), HPMA and ETMA (ethylenetriclycol methacrylate) (nonfunctional) as co-monomers. These nonfunctional monomers show a lower degree of conversion in fotoactivated systems and are able to reduce total contraction. However, according to Labella, et al.¹⁰, HPMA has to be added in approximately 40% in weight to be considered a good mixture with BISGMA and, at this level,

volumetric contraction is promoted. The content of low viscosity monomers and the low filler content may contribute to the high shrinkage level of the Solitaire resin. Watts and Hindi¹⁹ concluded that a lower initial contraction may be achieved either by special light irradiation regimes (low to high, or ramped) or in favorable cases by novel monomer-composite formulations and setting chemistry (e.g. Solitaire). In other words, these authors consider that light-activation at high intensity would promote the same effect as short-term or low-intensity irradiation in conventional BISGMA-based resins.

Alert, with 84% of filler, showed 2.33% contraction, significantly higher (±15%.) than that of SureFil. The matrix

TABLE 1- Characteristics of the composite resins evaluated in this study

Resins	Manufacturer	Matrix	Filler	Weight*
Filtek Z 250 (high)	3M ESPE (St. Paul, MN – USA)	BISGMA BISEMA UEDMA	Zirconium/SiO ₂ (synterized)	78%
Solitaire (medium)	Heraus/Kulzer (GmbH, Bad Homburg – Germany)	Silicium tetraacrylate BISGMA HPMA ETMA	(BFBaAl)SiO ₄ porous SiO ₂ SiO ₂	66%
ALERT(high)	Jeneric/Pentron Incorporated (Wallingford, CT –USA)	BISGMA ethoxylated	(BaAl) ₂ SiO ₄ SiO ₂ -MgO ₂ Al ₂ O ₃ -Si	84%
Suprafill (medium)	SSWhite (Rio de Janeiro – RJ – Brasil)	BISGMA TEGMA UEDMA	Ba ₂ SiO ₄	76,5%
Fill Magic (high)	Vigodent (Rio de Janeiro – RJ – Brasil)	BISGMA TEGMA BISEMA UEDMA	Ba ₂ SiO ₄ Sr ₂ SiO ₄ SiO ₂ Fluorets	81%
Surefil (high)	Dentsply (Eatontown – NJ – USA)	BISGMA TEGMA UEDMA	(BoFBaAl)SiO ₄ SiO ₂	82%
Definite (high)	Degussa (Dental Centrum Hanau – Germany)	Silicium dimethacrylate (Omorcer) Dimethacrylates	Ba ₂ SiO ₄ SiO ₂ Modified apatite	77%

*: inorganic filler %weight as informed by the manufacturer.

of the Alert resin is based on ethoxylated BISGMA. Due to its low viscosity, this monomer has some more polymerization degrees of freedom than BISGMA. Even the use of the fibers that manufacturers recommend to interweave within monomers to improve the material's strength cannot compensate the greater intimacy among free radicals, leading to a higher contraction.

The matrixes of Fill Magic (BISGMA, BISEMA, UEDMA and TEGMA), Surefil resin (BISGMA, TEGMA and UEDMA) and Filtek Z250 (BISGMA, BISEMA and UEDMA) have in common the main monomer, BISGMA. These resins showed at medium filler-content levels also an intermediate shrinkage. However, it is difficult to determine the conversion rate of each material without knowing proportions of the mixture (4). Therefore, it is difficult to determine the effects of the mixtures of BISGMA, TEGMA, BISEMA and UEDMA on the mechanical properties of these resins.

Filtek Z250 (3M) has in its matrix UEDMA (urethaneethylenedimethacrylate) and BISEMA, two monomers of different viscosities when compared to TEGMA. The extension of contraction, among other factors, depends on the molecular degree of freedom and on the functionality of monomers of the resin complex to form the composite resin matrix (14). Comparing the monomers of similar viscosity, the polymerization shrinkage increases with their functionality and, when comparing monomers with the same functionality, the polymerization shrinkage increases as the viscosity decreases. Consequently, the dilution of BISGMA increases the polymerization contraction¹⁵. TEGMA, due to its long and flexible chain, is often selected as a diluent of BISGMA, in such a way that the resulting mixture will have plasticity, resulting in optimal handling characteristics of the resin without reducing the material's strength or hardness. Alternatively, urethaneacrylates can be added to the resins to improve their resistance to wear and to reduce their absorption of water. However, a total replacement of TEGMA by UEDMA leads to a decrease in the elasticity modulus, in flexural strength and in tensile strength. This is possibly associated to the capacity of urethaneacrylate resins to form hydrogenionic links with

copolymers which, presumably, restricts the mobility of polymers³.

Recently, multiacrylate monomers have been used to replace the common dimethacrylates. Definite composite resin has a silicon organic matrix linked to methacrylate radicals and siloxanes (Si-O-Si). This molecule may work in two directions. First as an organic filler and second as a low degree-of-freedom-monomer. This can explain, in part, the lower volumetric contraction rate presented by Definite resin.

In the present study the lowest values of contraction were found for Suprafill, which could be attributed to the relation of BISGMA and diluents, or others factors. Further studies about filler type and shape also than initiation system have to be carried out.

The resins that have EBISGMA (ethoxylated-BISGMA) as basic monomer present a great filler content. The matrix has at least 20% less monomer and usually requires a higher amount of diluters to improve the handling characteristic of the material, which affect the volumetric contraction.

EBISGMA is a less viscous molecule than BISGMA and, thus, has more degrees of freedom. Consequently, it has a greater conversion rate and greater plasticity. On the other hand, it will have an increased contraction during the polymerization process. The water absorption in hydrophobic monomers is reduced, preventing the required hygroscopic expansion. For this reason, it is possible that resins containing EBISGMA may show a greater and more significant contraction than BISGMA-based resins. However, Surefil (with 82% filler), showed 2.01% of shrinkage, which is similar to other BISGMA-based resins. This demonstrates that volumetric contraction depends on the resin-filler complex that forms the resin and only a well-balanced mixture will produce a satisfactory and adequate product.

This study presented only one basic aspect of the polymerization contraction. Although it unquestionably depends on the basic monomers present in the matrix, there are also other external factors that should be studied in order to obtain the real value for polymerization contraction. The authors believe that possible influences on the volumetric shrinkage could be the conversion rate, filler type and shape, and cavity configuration. However, the composite resins evaluated in this study showed significantly different shrinkage values and the null hypothesis is therefore rejected.

TABLE 2- Volumetric polymerization shrinkage of the tested composite resins (n=5)

Group	Means (standard deviations)
Suprafill	1.8696 a (0.0084)
Definite	1.8921 a (0.0168)
Filtek Z250	1.9925 b (0.0327)
Surefil	2.0198 b (0.0646)
Fill Magic	2.1410 b (0.0525)
Alert	2.3299 c (0.0301)
Solitaire	2.9020 d (0.0482)

Different letters indicate statistically significant difference at 5%.

CONCLUSIONS

- The variability in polymerization shrinkage may be related to the differences in matrix formulation and filler content, type and shape.
- The percentage of volumetric polymerization shrinkage was smaller for Suprafill and Definite followed by Filtek Z250, while SureFil and Fill Magic showed intermediate values.
- The percentage of volumetric polymerization shrinkage was greater for Alert and Solitaire.

· Knowing the polymerization shrinkage rates of the commercially available composite resins, the dentist would be able to choose between using composite resins with lower polymerization shrinkage rates or adopting technical or operational procedures to minimize the adverse effects deriving from resin contraction during light-activation.

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